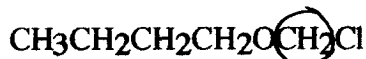


Name key
Chem 227 / Dr. Rusay / Exam 1

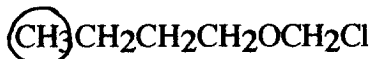
Note: In questions where there are more than one possible answer, the number of wrong answers will be deducted from the number of correct answer(s).

- 1) [4pts] If all the protons of the following compound could clearly be discerned in the spectrum,
a) which proton(s) would you expect to be at the lowest field in the ^1H NMR spectrum?
(Circle the correct answer.) *- farthest downfield*



V IV III II I

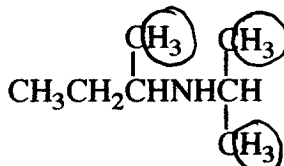
- b) which proton(s) would you expect to be at the highest field in the ^1H NMR spectrum?
(Circle the correct answer.)



V IV III II I

- 2) [2pts] How many signals would you expect to find in the ^1H NMR spectrum of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$? 2

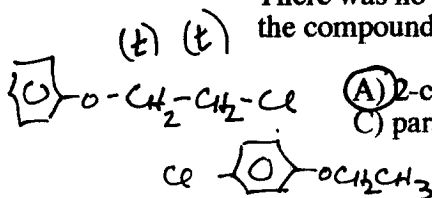
- 3) [2pts] Circle any proton(s) in the compound which would appear as a doublet in the ^1H NMR spectrum.



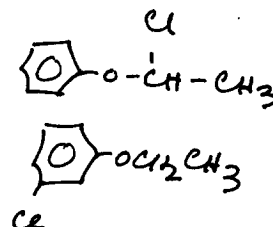
- 4) [4pts] A compound with the molecular formula $\text{C}_8\text{H}_9\text{ClO}$ gave the following ^1H NMR spectrum:

triplet, 3.7 ppm
triplet, 4.2 ppm
multiplet, 7.1 ppm

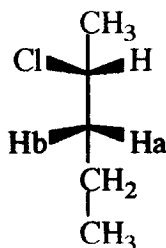
There was no evidence of an -OH band in the IR spectrum. The most likely structure for the compound is:



- (A) 2-chloro-1-phenoxyethane
(C) para-chlorophenoxyethane
(B) 1-chloro-1-phenoxyethane
(D) meta-chlorophenoxyethane
(E) meta-chlorophenoxyethane



- 5) [3pts] In the following compound protons a and b are:

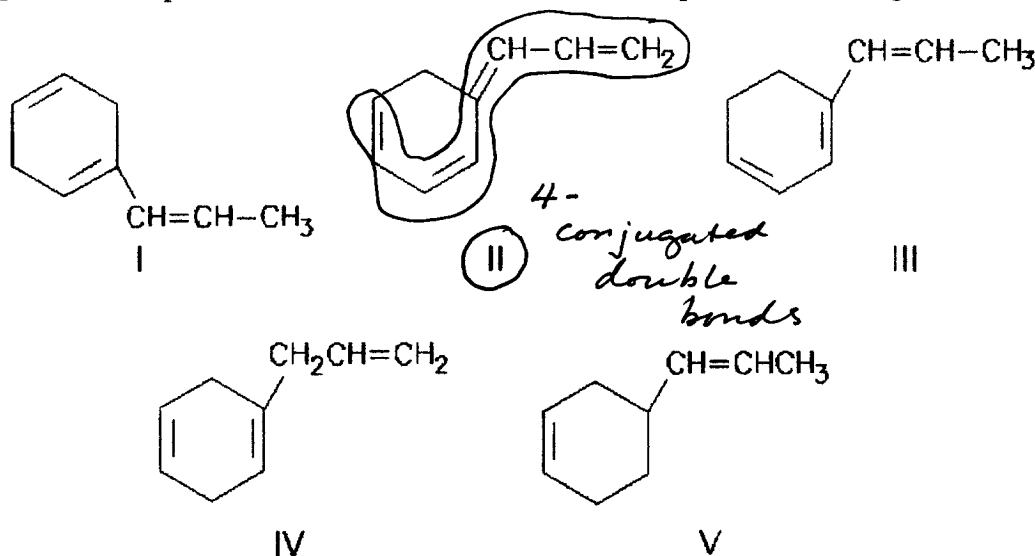


- A) Identical
B) Enantiotopic
C) Diastereotopic
D) Homeopathic
E) Mesotopic

6) [4pts] a) How many ^{13}C signals will 1,3-dichlorobenzene produce in its nmr spectrum? 4

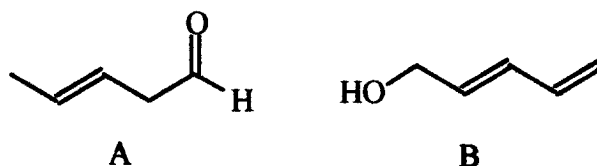
b) How many doublets will be observed in its ^{13}C nmr spectrum? 3

7) [3pts] Which compound would have a UV maximum absorption band at longest wavelength?



8) [2pts] An oxygen-containing compound which shows no IR absorption at $1630\text{--}1780\text{ cm}^{-1}$ or at $3200\text{--}3550\text{ cm}^{-1}$ is likely to be what type of compound (i.e. its chemical functionality)? ether

9) [3pts] Clearly describe how mass spectroscopy can distinguish between the following structural isomers. Be sure to provide m/e peak values for each compound's fragments to support your explanation.



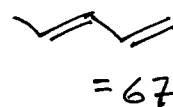
Description:

Molecular ion: $\text{C}_5\text{H}_8\text{O} = 60 + 8 + 16 = 84$

$m-1 = 84-1 = 83$
 (H)

$m-17 = 67$
 (-OH)

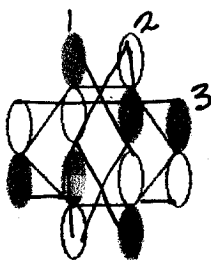
$m-29 = 55$
 ($\text{H}-\text{C}\equiv\text{O}^+$)



$\text{CH}_2 = 55$

10) [2pts] In the molecular orbital model of benzene, the six p-orbitals combine to form how many molecular orbitals? 6

11) [4pts] a) Draw and number all of the nodal planes in the following m.o. drawing.

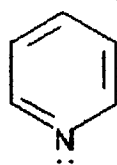


—
— —
— —
—
HOMO
LUMO
HOMO
LUMO

b) Identify the above m.o.'s energy level, eg. HOMO, LUMO, etc.

HOMO

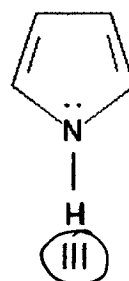
12) [6pts] Circle all of the aromatic ions and compounds. (NOTE: Question will be graded # right minus # wrong.)



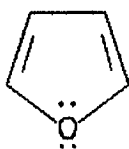
I



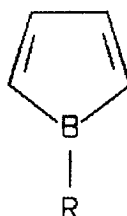
II



III



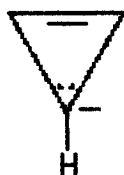
IV



V



VI



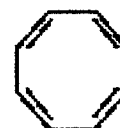
VII



VIII



IX



X



10e⁻

XI

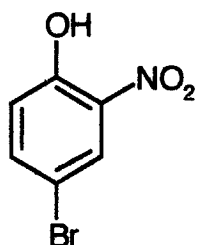


XII



XIII

13) [3pts] Name the following compound:



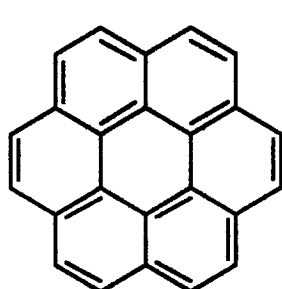
4-bromo-2-nitrophenol

14) [5pts] The following unsaturated carbon ring compounds have their topological resonance energies given per pi electron. List the compounds in order of increasing stability and identify each as being aromatic (a) or anti-aromatic (aa) or non-aromatic (na). eg. F(aa)

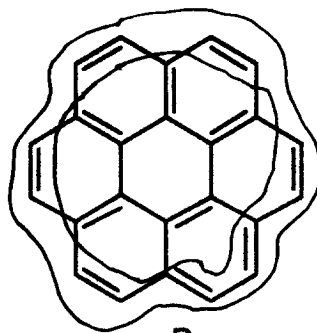
- A) 1,3-cyclohexadiene (~ 0.000)
- B) pentalene (-0.0269)
- C) benzene (0.0454)
- D) cyclooctatetraene (-0.0744)
- E) pyrene (0.0374)

D(aa) < B(aa) < A(na) < E(a) < C(a)

15) [4pts] Coronene is a planar compound. Using Huckel's rule and the two resonance forms of coronene below, explain if you expect coronene to be aromatic or not and why.



A



B

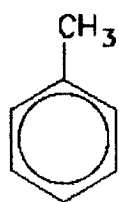
$$4n + 2$$

$$4(3) + 2 = 14e^-$$

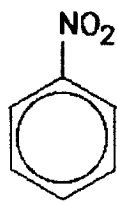
Explanation:

24 πe^- s TOTAL DOES NOT SATISFY
HUCKEL'S RULE, BUT B HAS
14 πe^- s in a plane on the
ring's PERIMETER WHICH MAKES
IT AROMATIC.

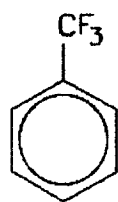
16) [5pts] Rank the following compounds in the order of highest reactivity to the lowest for electrophilic aromatic substitution.



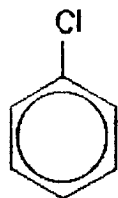
I



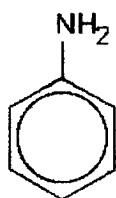
II



III

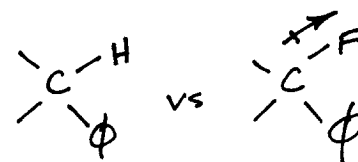


IV

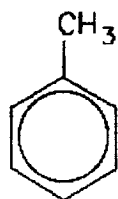


V

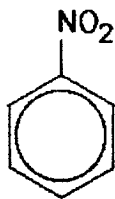
V > I > III > IV > II



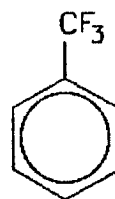
17) [5pts] Indicate the possible substitution position(s) [ortho, meta, para] for the product(s) formed from each of the following compounds:



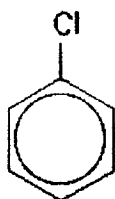
I



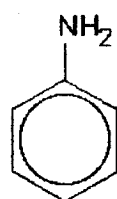
II



III



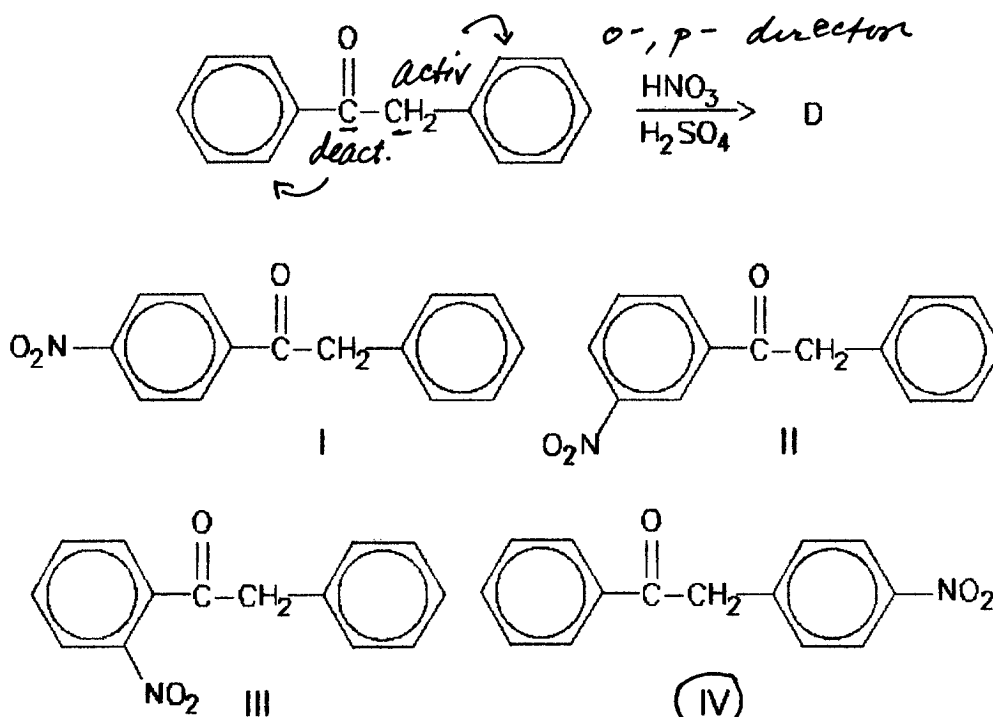
IV



V

I o-, p-
 II m
 III o-, p-
 IV o-, p-
 V o-, p-

18) [4pts] The major product(s) D of the following reaction would be:



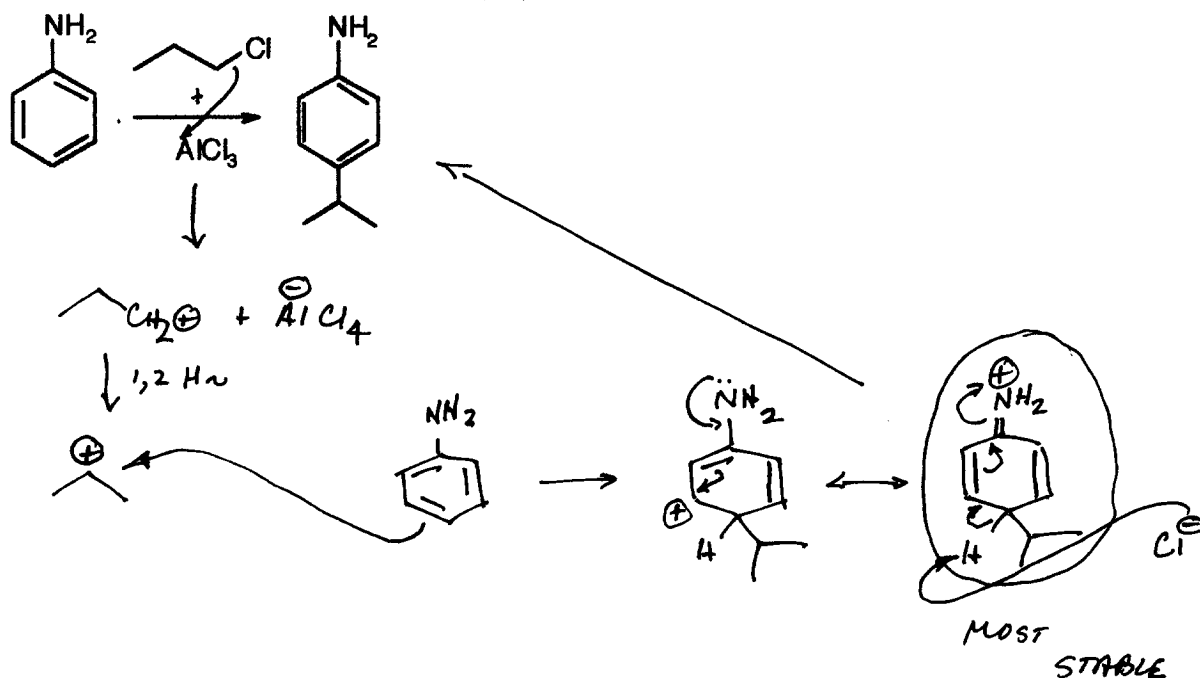
A) I B) II C) III **(D) IV** E) Approximately equal amounts of I and II

20) [3pts] Which molecule cannot participate as a reactant in a Friedel-Crafts alkylation reaction?

A) Benzene B) Chlorobenzene **(C) Nitrobenzene**
 D) Toulene E) Salicylic acid (o-hydroxybenzoic acid)

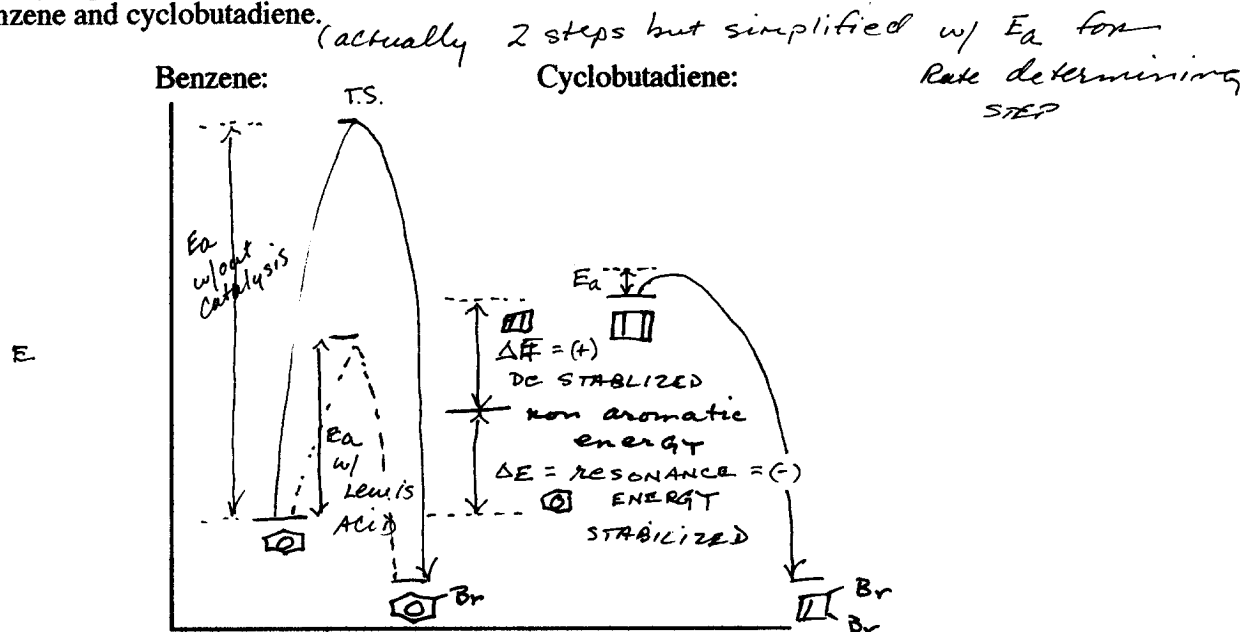
21) [9pts] The following reaction is a Friedel-Crafts alkylation. Illustrate the mechanism including the formation of the electrophile and indicate the most stable resonance contributor for the Arenium ion.

Mechanism with resonance structure:



22) [9pts] Benzene reacts with bromine only in the presence of a Lewis acid. If the general reactivity of benzene were compared to the reactivity of cyclobutadiene, cyclobutadiene is much more reactive.

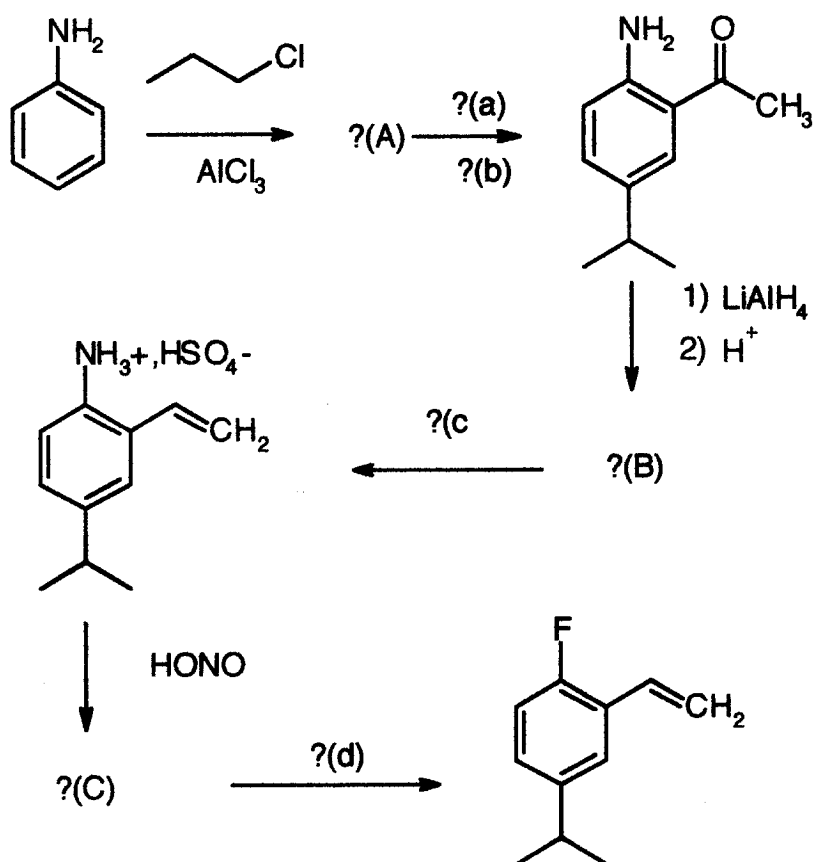
Illustrate the relative reactivities of the two compounds using an energy diagram. Show the relative energies of activation and the effect of a Lewis acid on the E_a for benzene. Be sure to indicate what is "resonance energy" on the diagram. (Note: The comparison is NOT to be in absolute, quantitative terms. Illustrate the relative differences graphically as a qualitative comparison.) Briefly explain the differences in reactivity in terms of resonance stabilization energy between benzene and cyclobutadiene.



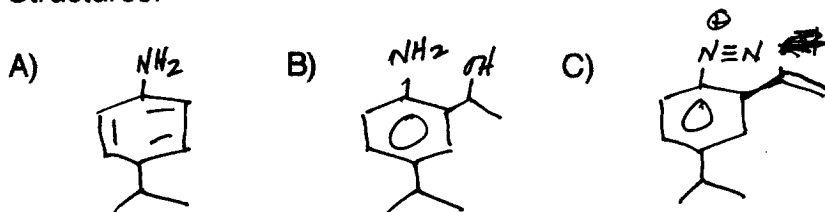
Explanation:

- (1) c1ccccc1 + Br2 -> c1ccccc1Br
 very high E_a which Lewis acid (catalyst) lowers, the reactivity of c1ccccc1 is very high $\therefore E_a$ very low.
- (2) c1ccccc1 $\Delta E = (-)$ relative to compound which does not have resonance stabilized aromaticity (non aromatic)
- c1ccccc1 $\Delta E = (+)$ relative to compound THAT is Non Aromatic.

23) [14pts] Provide the three structures (A), (B) and (C), and the four reagents (a), (b), (c) and (d) in the following reaction scheme.



Structures:



Reagents:

a) CH_3COCl

b) AlCl_3

c) H_2SO_4

d) HBF_4